



Vailable online at www.sciencedirect.com
SciVerse ScienceDirect

Energy Procedia 27 (2012) 70 – 75

Energy
Procedia

SiliconPV: April 03-05, 2012, Leuven, Belgium

Light induced degradation in mc-Si based on compensated silicon

R Søndena^{a*}, A.-K. Søiland^b, H. Angelskår^a, A. Holt^a

^a*Institute for Energy Technology, P.O.Box 40, N-2027 Kjeller, Norway*

^b*Elkem Solar AS, P.O.Box 8040, N-4675 Vågsbygd, Norway*

Abstract

Light induced degradation caused by boron-oxygen related defects in boron doped Czochralski silicon is known to considerably reduce the solar cell conversion efficiency upon initial use. In multicrystalline silicon the minority carrier lifetime is determined by grain boundaries, twins, dislocations as well as intentional and unintentional contaminants. In addition to metallic impurities such as iron, chromium and copper, which are known to degrade the lifetime under illumination, boron doped multicrystalline silicon also contains oxygen. With increasing quality of the silicon feedstock BO-related degradation is becoming an increasingly important factor limiting the lifetime in multicrystalline wafers. Using photoluminescence-imaging the light induced degradation in mc-Si wafers based on compensated silicon are studied. High resolution lifetime maps allow for a spatial evaluation of the degradation across wafers.

© 2012 Published by Elsevier Ltd. Selection and peer-review under responsibility of the scientific committee of the SiliconPV 2012 conference. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Compensated silicon; multicrystalline silicon; light induced degradation

1. Main text

Two main causes have been identified for the light induced degradation of solar cells based on boron-doped Czochralski (Cz) and multicrystalline (mc) silicon; Formation or activation of boron-oxygen-complexes and dissociation of iron-boron-pairs into isolated interstitial iron, Fe_i, and substitutional boron, B_s. Light induced degradation (LID) due to boron-oxygen related defects limits the lifetime in, and thus

* Corresponding author. Tel.: +47 63806471; fax: +47 63812905
E-mail address: rune.sondena@ife.no

the performance of solar cells based on boron doped Cz-wafers. Silicon solar cells containing both oxygen and boron can lose as much as 10% of the initial efficiency during operation [1]. This effect has been attributed to the B_iO_2 -complex [2]. The recombination activity of the BO-complex is enhanced when charge carriers are generated in the material either by illumination or by applying a bias voltage [3-5]. Fe_i will together with B_s form FeB-pairs in silicon. High intensity illumination dissociates these FeB-pairs into separate Fe_i and B_s atoms within minutes [6, 7]. The FeB-pairs will re-form when stored in the dark at room temperature for 24 hours. Unlike the BO-complexes these iron-boron related defects are highly dependent on the minority carrier injection level [8, 9].

It is well known that BO-complexes considerably degrade and limit the lifetime in boron doped Cz-Si containing oxygen, while in mc-Si wafers metallic impurities as well as the grain boundaries and dislocations have been considered the main limitations of the performance. However, the quality of silicon feedstock, including compensated feedstock, is continuously improving. Optimized silicon crystallization and solar cell processes tailored to minimize the effects of metallic impurities together with the improved quality of multicrystalline wafers make degradation due to boron-oxygen complexes increasingly important. Multicrystalline silicon also contains oxygen, and similar behavior in both Cz- and mc-Si under illumination has previously been reported [10]. Relative efficiency losses due to LID in boron doped mc-Si solar cells has been reported to be 2-3% in oxygen rich wafers [11], and 1-1.5% in wafers containing different degrees of compensation [12].

In the present work LID in mc-Si is studied using photoluminescence (PL) imaging. The high resolution PL-images allow for a spatial evaluation of different areas of the wafers. The defects limiting the lifetime in the wafers are then discussed.

2. Experimental details

Multicrystalline silicon wafers based on compensated feedstock made by two different producers, P1 and P2, are compared. Wafers from bottom, center and top of ingots consisting of 0% (REF), 60-65% and 100% compensated silicon have been studied with respect to light induced degradation. The resistivities range from 0.7 to about 1.5 Ω -cm. All wafers are phosphorous diffusion gettered. After an initial damage removal in a HNA-solution, gettering is performed in a $POCl_3$ tube furnace. A 50 Ω/\square phosphorus emitter in-diffusion is followed by an emitter etch back. The surfaces are passivated using hydrogenated amorphous silicon deposited in a PECVD chamber. Light induced degradation is achieved by illuminating the wafers with an intensity of 1 Sun (100 mW/cm²) using a Xenon lamp. The initial lifetime was measured immediately after an annealing, while the stable degraded lifetime is measured after 24 hours of illumination.

Lifetime maps were obtained using photoluminescence imaging [13]. A diode laser with a wavelength of 808 nm is used to illuminate the entire wafer and the resulting band-to-band PL-signal is measured with a charge-coupled device camera. The intensity of this PL-signal scales with the number of excited minority charge carriers. A separate QSSPC calibration measurement is carried out to convert the PL-intensity into absolute charge carrier density [14]. Assuming uniform doping and optical properties the variations in the signal reflects the minority carrier lifetime across the sample. All measurements are performed at a fixed generation equivalent to 1 Sun illumination, i.e. the injection level varies with material quality. High lifetime areas will be in higher injection than areas with lower lifetimes, resulting in an overestimation of the high lifetimes and, thus, the normalized defect concentration, N_t^* . Photoluminescence is also used for Fe-mapping of the gettered wafers.

Table 1. Resistivities estimated from QssPC measurements

Wafers	Resistivity [$\Omega\text{-cm}$]
P1-60%	1.1 – 1.5
P2-65%	1.1 – 1.4
P1-100%	1.1 – 1.4
P2-100%	0.7 – 0.8
REF (P1)	1.2 – 1.4

3. Results and discussion

PL-imaging is used to study the lifetime in multicrystalline silicon wafers from two different producers. The wafers, based on compensated silicon, are all phosphorus gettered and surface passivated. Average minority carrier lifetimes before (annealed) and after (degraded) light induced degradation of gettered wafers are presented in Figure 1a). Measurements show comparable lifetimes for 60-65% and 100% compensated silicon. Average lifetimes range from 50 to 170 μs after annealing, while the degraded lifetimes range from 30 to 130 μs . The lifetime in the reference wafer from the bottom position is somewhat higher. Figure 1b) shows the normalized defect concentrations, $N_t^* = \tau_{\text{degraded}}^{-1} - \tau_{\text{annealed}}^{-1}$, averaged over the surfaces. Highest defect concentration is found in P2-100%. However, it should be noted that the P2-100% wafers have lower resistivity, i.e. they contain more boron than the other wafers series. Recent studies on compensated Cz-Si show that the LID scales with the net doping and not the total boron concentration [15, 16]. Increased LID in P2-100 corresponds well with findings from monocrystalline silicon. Wafers from P1-100% have resistivity comparable to the wafers containing 60-65% compensated silicon and show comparable degradation. The oxygen contents in the wafers are not determined but assumed comparable. In addition to low defect density P1-100% also show high lifetimes despite the increased content of compensated feedstock. For center and top positions P1-100% shows higher lifetimes than the corresponding reference wafers. The high lifetimes observed in P1-100% may be attributed to beneficial effects of the phosphorous contribution, e.g. an injection level effect or a Fermi level shift [17, 18].

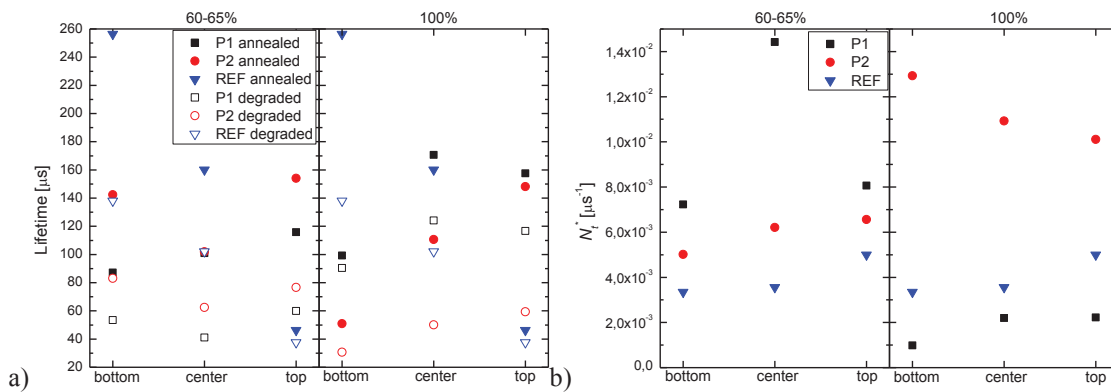


Fig. 1. Average lifetimes measured using QssPC-calibrated photoluminescence-imaging for annealed (closed symbols) and degraded (open symbols) wafers are shown in a). Normalized defect concentrations are presented in b). Note that P2-100% contains somewhat more boron. Wafers containing 60-65% and 100% compensated silicon are presented as well as the non-compensated reference

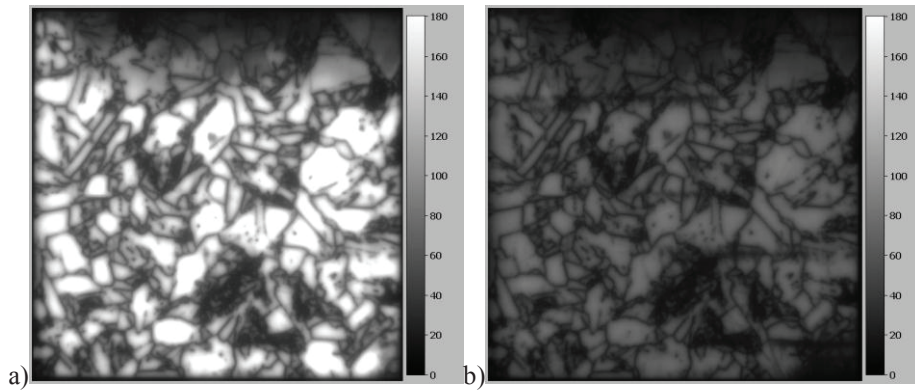


Fig. 2. PL-image of P1-60% center wafer a) in the annealed state and b) degraded after 24 hours of illumination. The scales are in μs

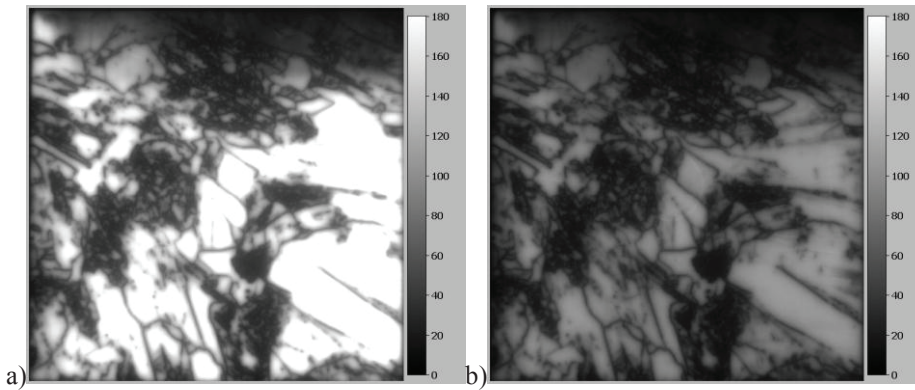


Fig. 3. PL-image of P2-100% center wafer a) in the annealed state and b) degraded after 24 hours of illumination

The light induced degradation is also illustrated by the PL-images. Figures 2 and 3 show the annealed and the degraded lifetime for the center wafers of P1-60% and P2-100%, respectively. The PL-images also show the lifetime variations across the wafers. The high resolution of the images allows for a more detailed study of the lifetime and the degradation. Smaller areas with a more uniform lifetime are compared. High lifetime areas with large, dislocation free grains and low lifetime areas with higher dislocation densities are chosen. Note that there are still large differences between the areas studied in the different wafers. The normalized defect concentration is again calculated for smaller areas corresponding to high and low lifetime areas (Fig. 4a). In addition to the differences in lifetime the different areas of the wafers show degradation of different magnitude. According to the defect concentrations the low lifetime areas show more degradation than the high lifetime areas, despite the lower initial lifetime. The defect concentration is typically 5 times larger in areas with small grains. However, this is mainly caused by the low initial lifetime in eq. 2. Figure 4b shows that the degradation relative the initial lifetime is larger in high lifetime areas. Despite the different nature of the high and low lifetime areas the time scale of the degradation is comparable. The lifetime degrades towards a stable lower limit during several hours. This is consistent with LID caused by BO-complexes as seen in Czochralski-wafers [15, 16] and with previous studies [10, 11].

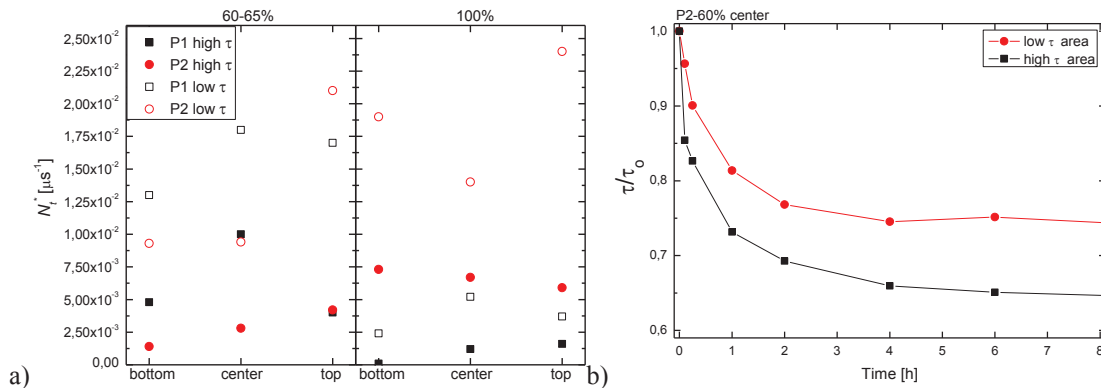


Fig. 4. Normalized defect concentrations in high- and low-lifetime areas for wafers containing 60-65% and 100% compensated silicon are presented in a). Degradation of the lifetime relative the initial annealed lifetime is shown in b)

Phosphorus diffusion gettering is known to remove metallic impurities quite well in dislocation free areas with large grains. However, in low lifetime areas with high dislocation densities gettering is less efficient [19, 20]. Grain boundaries and dislocations tend to attract and trap impurities, rather than allowing the phosphorus emitter to extract them to the surface where they do less damage. A higher concentration of metallic impurities, such as iron, as well as oxygen accumulation is therefore expected in the low lifetime areas. Oxygen from the dislocation rich areas might still be able to form light sensitive defect complexes responsible for LID also in the low lifetime areas.

Mapping of the iron content is performed by splitting the iron-boron-pairs with high intensity illumination for one minute. Virtually no difference between the FeB and Fe_i limited lifetime, before and after illumination, is observed. The effect of iron on the lifetime is minimal after gettering. The effect of degradation due to iron is also expected to occur within minutes. Figure 4b) shows that the degradation takes place over several hours. It is therefore reasonable to assume that mainly boron-oxygen related complexes, rather than iron-boron-pairs are responsible for the degradation in both the high- and low-lifetime areas.

4. Summary

Multicrystalline wafers from two producers containing different amounts of compensated silicon have been examined. The defect concentrations in the compensated wafers are comparable to the non-compensated reference, and no increase in LID is observed with increasing content of compensated silicon. However, decreased resistivity, i.e. increased net doping, results in an increase in degradation. The wafers are degraded using an illumination of 1 Sun, and PL-imaging is used to investigate the lifetime across the wafers. Smaller areas with more uniform lifetime distributions are studied. Both in areas with high dislocation densities and in areas with large grains the light induced degradation occur within hours of illumination, in good accordance with degradation caused by BO-complexes. Since the magnitude of the degradation also seems to depend on the boron concentration it is assumed that the degradation in these multicrystalline wafers is predominantly caused by BO-related defects. Oxygen may agglomerate in areas with high densities of crystal imperfections, but is still able to form BO-complexes degrading the lifetime upon illumination.

References

- [1] K. Bothe, J. Schmidt, Electronically activated boron-oxygen-related recombination centers in crystalline silicon, *J. Appl. Phys.* 99 (2006) 013701.
- [2] V.V. Voronkov, R. Falster, Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells, *J. Appl. Phys.* 107 (2010) 053509.
- [3] B. Lim, F. Rougieux, D. Macdonald, K. Bothe, J. Schmidt, Generation and annihilation of boron-oxygen-related recombination centers in compensated p- and n-type silicon, *J. Appl. Phys.* 108 (2010) 103722.
- [4] A. Herguth, G. Hahn, Boron-oxygen related defects in Cz-silicon solar cells-degradation, regeneration and beyond, in: 24th EUPVSEC, Hamburg, Germany, 2009.
- [5] A. Herguth, G. Schubert, M. Kaes, G. Hahn, Investigations on the long time behavior of the metastable boron-oxygen complex in crystalline silicon, *Prog. Photovolt: Res. Appl.* 16 (2008) 135.
- [6] M. Wilson, P. Edelman, A. Savtchouk, J. D'Amico, A. Findlay, J. Lagowski, Accelerated light-induced degradation (ALID) for monitoring of defects in PV silicon wafers and solar cells, *J. Electron. Mater.* 39 (2010) 642.
- [7] L.J. Geerligs, D. Macdonald, Dynamics of light-induced FeB pair dissociation in crystalline silicon, *Appl. Phys. Lett.* 85 (2004) 5227.
- [8] D. Macdonald, J. Tan, T. Trupke, Imaging interstitial iron concentrations in boron-doped crystalline silicon using photoluminescence, *J. Appl. Phys.* 103 (2008) 073710.
- [9] D.H. Macdonald, L.J. Geerligs, A. Azzizi, Iron detection in crystalline silicon by carrier lifetime measurements for arbitrary injection and doping, *J. Appl. Phys.* 95 (2004) 1021.
- [10] D.H. Macdonald, L.J. Geerligs, S. Riepe, Light-induced lifetime degradation in multicrystalline silicon, in: 13th workshop on crystalline silicon solar cell materials and processes, Colorado, USA, 2003.
- [11] M. Sheoran, A. Upadhyaya, A. Rohatgi, A comparison of bulk lifetime, efficiency, and light-induced degradation in boron- and gallium-doped cast mc-Si solar cells, *IEEE Trans. Electron Dev.* 53 (2006) 2764.
- [12] K. Peter, R. Kopecek, M. Wilson, J. Lagowski, E. Enebakk, A.-K. Soiland, S. Grandum, Multicrystalline solar grade silicon solar cells, in: 35th IEEE PVSC, Honolulu, Hawaii, USA, 2010.
- [13] T. Trupke, R.A. Bardos, M.C. Schubert, W. Warta, Photoluminescence imaging of silicon wafers, *Appl. Phys. Lett.* 89 (2006) 044107.
- [14] S. Herlufsen, J. Schmidt, D. Hinken, K. Bothe, R. Brendel, Photoconductance-calibrated photoluminescence lifetime imaging of crystalline silicon, *Phys. Status Solidi (RRL)*, 2 (2008) 245.
- [15] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, L.J. Geerligs, Light-induced boron-oxygen defect generation in compensated p-type Czochralski silicon, *J. Appl. Phys.* 105 (2009) 093704.
- [16] J. Geilker, W. Kwapil, S. Rein, Light-induced degradation in compensated p- and n-type Czochralski silicon wafers, *J. Appl. Phys.* 109 (2011) 053718.
- [17] S. Dubois, N. Enjalbert, J.P. Garandet, Effects of the compensation level on the carrier lifetime of crystalline silicon, *Appl. Phys. Lett.* 93 (2008) 032114.
- [18] D. Macdonald, A. Cuevas, Recombination in compensated crystalline silicon for solar cells, *J. Appl. Phys.* 109 (2011) 043704.
- [19] A. Bentzen, A. Holt, R. Kopecek, G. Stokkan, J.S. Christensen, B.G. Svensson, Gettering of transition metal impurities during phosphorus emitter diffusion in multicrystalline silicon solar cell processing, *J. Appl. Phys.* 99 (2006) 093509.
- [20] A. Bentzen, A. Holt, Overview of phosphorus diffusion and gettering in multicrystalline silicon, *Mater. Sci. Eng. B* 159-160 (2009) 228.